

IONIC INTERACTIONS IN BIOPOLYMER GELS

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The interaction of polyelectrolytes with oppositely charged ions is an active area of research in diverse fields of science. In polymer physics and materials science it is related to general problems of phase transition and polyelectrolyte behavior. In biology and medicine it is motivated by the need to understand the mechanisms of packaging genetic information, e.g., for developing new therapeutic methods of delivering genes to the target cells. Although previous studies have shown that ions exert a strong influence on the osmotic pressure of polyelectrolyte solutions, less attention has been paid to the biologically relevant case when both mono- and divalent ions are present.¹ Monovalent-divalent cation exchange plays an important role in certain physiological processes such as nerve excitation and muscle contraction. For example, the step-like nature of the volume transition induced by $\text{Ca}^{2+}/\text{Na}^+$ exchange in sodium polyacrylate (PAANA) hydrogels has attracted interest as a physico-chemical model for describing nerve excitation.²

When Ca^{2+} ions are introduced into PAANA solutions above a certain $\text{Ca}^{2+}/\text{Na}^+$ ratio phase transition occurs.³ Anomalous x-ray scattering measurements⁴ as well as molecular dynamics simulations⁵ indicate that divalent counterions interact in closer proximity with the oppositely charged polyelectrolyte chains than monovalent counterions. In systems in which monovalent and divalent ions coexist, such as physiological salt solutions, it is unclear how these ions contribute to the osmotic and electrostatic interactions. The characteristics of the phase transition induced by monovalent/divalent ion exchange may be significantly different from that induced by changing the temperature, pH or solvent composition. Osmotic pressure measurements show that the presence of divalent ions produces a pronounced variation in the third virial coefficient of the osmotic pressure, while the second virial term remains practically unchanged.⁶

We demonstrate that DNA exhibits osmotic and scattering properties remarkably similar to those of PAANA. An important common feature of DNA and PAANA is that the backbone of both polymers is hydrophobic. Polymers with hydrophobic backbones precipitate when the electrostatic interactions are compensated. We contrast the properties of DNA to those of charged polysaccharides (hyaluronic acid, chondroitin sulfate, etc.). Polysaccharides differ from the other types of biopolymer in the following ways:

- The backbone of polysaccharides is hydrophilic, unlike polynucleic acids, which are hydrophobic.
- Polysaccharides are homopolymers, while polynucleic acids and proteins are copolymers.
- Polysaccharide molecules display chain rigidity (long persistence length), unlike proteins, which are flexible.

The consequences of the above differences on the molecular organization, interactions and functional properties will be discussed.

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References

- (1) Flory, P.J.; Osterheld, J.E. *J. Phys. Chem.* **1954**, *58*, 653.
- (2) Tasaki, I.: On the Reversible Abrupt Structural Changes in Nerve Fibers Underlying Their Excitation and Conduction Processes. In *Phase Transitions in Cell Biology*. Eds. G. H. Pollack, and W. C. Chin, Springer Science, 1-21, 2008.
- (3) Horkay, F.; Tasaki, I.; Basser, P.J. *Biomacromolecules* **2000**, *1*, 84.
- (4) Horkay, F.; Hecht, A.M.; Rochas, C.; Basser, P.J.; Geissler, E. **2006**, *J. Chem. Phys.* *125*, 234904 (2006).
- (5) Yin, D.W.; Horkay, F.; Douglas, J.F.; De Pablo, J.J. *J. Chem. Phys.* **2008**, *129*, 154909.
- (6) Horkay, F.; Basser, P.J.; Hecht, A.M.; Geissler, E. *Macromol. Biosci.* **2002**, *2*, 207.